Simulation of hydrogen diffusion and boron passivation in crystalline silicon

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Abstract. The model of hydrogen migration and of the reactions of hydrogen atoms with electrically active impurity, developed earlier, has been applied to simulate hydrogen diffusion and passivation process during plasma deuteration of silicon substrates doped with boron. The calculated deuterium concentration profiles agree well in the length of the passivated region with the experimental data obtained on treatment in hydrogen plasma at a temperature of 200 °C for 5, 10, and 15 minutes. On the other hand, to achieve a good fit to the abruptness of the calculated profiles between the passivated and unpassivated regions, it is necessary to suppose that the values of the parameters that describe the absorption of hydrogen interstitials by electrically active dopant atoms decrease with increase in the depth of the passivated region. For example, nonuniform spatial distributions of nonequilibrium point defects generated during plasma treatment can lead to a spatial dependence of hydrogen absorption.

Keyword: diffusion; passivation; interstitial; hydrogen; boron; silicon; solar cell
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1 Introduction

The increase in the cost of traditional energy resources has been a worldwide tendency during the past years. Therefore, investigation and implementation of alternative renewable energy sources are particularly urgent now. Solar cells provides such type of promising alternative energy sources. Here, new modules based on silicon layers constitute a reliable, proven, sustainable, and environmentally friendly source of energy. It is worth noting that the best crystalline silicon photovoltaic modules are 5 % more efficient than the best modules based on polysilicon films [1, 2]. It is especially important for solar cells used in outer space. The treatment of silicon photovoltaic layers in a hydrogen containing gas plasma results in a further increase in the solar energy-to-electricity conversion ratio. All of the above-mentioned factors demonstrate the importance of elucidating the role of hydrogen in the evolution of defect-impurity system in the near-surface region of silicon layers including passivation of dangling bonds, undesirable defects, and dopant atoms. The main goal of this work is to analyze theoretical models and carry out calculations

of hydrogen diffusion and hydrogen passivation of electrically active impurity atoms in silicon crystals doped with boron.

2 Model

The model of hydrogen diffusion with account for the passivation of electrically active impurity atoms was developed in [3, 4]. It is worth noting that in contrast to other models of hydrogen diffusion (see, for example, [5]), in the model of Velichko et al. [3, 4], as well as in the model of Zhang [6], the values of hydrogen diffusivity are approximated from high-temperature experimental diffusivity data obtained in [7]. Thus, the contradiction between the diffusivity data obtained for low- and high-temperature treatments (see [6] and references therein) is eliminated. It is supposed in [3, 4] that there are two fluxes of hydrogen atoms: "slow" diffusing hydrogen species, responsible for diffusion in the near-surface region with high a hydrogen concentration, and "fast" diffusing species, responsible for the hydrogen diffusion into the bulk of a semiconductor in the low-concentration region of the hydrogen concentration profile. It was supposed that the fast diffusion occurs due to the long-range migration of nonequilibrium interstitial hydrogen atoms in singly negatively (H^-), neutral ($H^\times$), and singly positively (H^+) charge states. Due to the high mobility of electrons (holes), the mass action law is valid for conversions between different charge states of hydrogen interstitials. The long-range migration of hydrogen interstitials results in the supersaturation of the bulk of a semiconductor with hydrogen atoms. Therefore, it is supposed in [3, 4] that these fast diffusing species are responsible for the passivation of electrically active boron atoms due to the following reactions:

$$A^- + H^+ \longrightarrow (AH)^\times \,, \tag{1}$$

$$A^- + H^\times \longrightarrow (AH)^\times + e^- \,, \tag{2}$$

where A^- is the acceptor atom in the substitutional position; $(AH)^\times$ is the neutral immobile "boron-hydrogen" complex, and e^- is the electron. Then, to calculate the total hydrogen concentration profile and concentration profile of the electrically active boron the following system of equations can be used:

1) the conservation law for trapped hydrogen atoms:

$$\begin{aligned} \frac{\partial C^{HTR}}{\partial t} &= \frac{k^{HIC}(\chi)\, C^{HI\times}(x,t)}{\tau_i^{HI}} \\ &+ k_i^{HIA} k^{HIAC}(\chi)\, C^{HI\times}(x,t) + S^{HT}(x,t) - G^{HT}(x.t)\,, \end{aligned} \tag{3}$$

2) the conservation law for substitutionally dissolved dopant atoms:

$$\frac{\partial C(x,t)}{\partial t} = -k_i^{HIA} k^{HIAC}(\chi) C\, C^{HI\times}(x,t)\,, \tag{4}$$

3) the stationary diffusion equation for nonequilibrium hydrogen interstitials:

$$\frac{\partial}{\partial x}\left[d_i^{HI} d^{HIC}(\chi)\frac{\partial\, C^{HI\times}(x,t)}{\partial x}\right] - \frac{k^{HIC}(\chi)}{\tau_i^{HI}}\, C^{HI\times}(x,t)$$
$$- k_i^{HIA} k^{HIAC}(\chi) C\, C^{HI\times}(x,t) + G^{HI}(x,t) = 0\,, \tag{5}$$

4) the diffusion equation for slow migrating hydrogen species:

$$\frac{\partial\, C^{HD}}{\partial\, t} = D_i^H \frac{\partial^2 C^{HD}}{\partial\, x^2} + G^{HD}\,, \tag{6}$$

where

$$d^{HIC}(\chi) = \frac{\beta^{HI-}\chi^{-1} + 1 + \beta^{HI+}\chi}{\beta^{HI-} + 1 + \beta^{HI+}}\,, \tag{7}$$

$$k^{HIC}(\chi) = \frac{\beta^{HIS-}\chi^{-1} + 1 + \beta^{HIS+}\chi}{\beta^{HIS-} + 1 + \beta^{HIS+}}\,, \tag{8}$$

$$k^{HIAC}(\chi) = \frac{1 + \beta^{HIA}\chi}{1 + \beta^{HIA}}\,, \tag{9}$$

$$\chi = \frac{C - C_B + \sqrt{(C - C_B)^2 + 4n_i^2}}{2n_i}\quad, \tag{10}$$

$$C^{HT} = C^{HTR} + C^{HD} + C^{HI}\,. \tag{11}$$

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Here C^{HT} is the total concentration of hydrogen atoms; C^{HTR} is the total concentration of the hydrogen atoms trapped by immobile sinks and boron atoms; C and C_B stand for the concentration of electrically active dopant atoms which undergo passivation and the concentration of charged species with the opposite type of conductivity, respectively; C^{HI} and $C^{HI\times}$ represent the total concentration of interstitial hydrogen atoms and the concentration of hydrogen interstitials in a neutral charge state, respectively; C^{HD} is the concentration of the slow diffusing hydrogen species; χ is the concentration of charge carriers (holes p or electrons n for passivation of acceptor or donor impurities, respectively) normalized to the concentration of intrinsic charge carriers n_i; S^{HT} and G^{HT} are respectively the rates of direct trapping and detrapping of hydrogen atoms introduced into the near surface region of silicon substrate by platelets or other extended defects; G^{HI} is the generation rate of nonequilibrium hydrogen interstitials in the surface region due to the plasma treatment and dissolution of platelets or other defects which incorporate hydrogen atoms; G^{HD} is the generation rate of hydrogen atoms participating in slow diffusion; d_i^{HI} and $d^{HIC}(\chi)$ are the diffusivity of hydrogen interstitials in an intrinsic semiconductor and normalized concentration dependence for diffusivity of this species in a doped semiconductor, respectively; D_i^{HD} is the diffusivity of the slow migrating hydrogen species; $\tau_i^{HI} = (k_i^{HI})^{-1}$ is the average lifetime of nonequilibrium hydrogen interstitials in an intrinsic semiconductor; k_i^{HI} and $k^{HIC}(\chi)$ are the coefficient of absorption of hydrogen interstitials in an undoped semiconductor and the normalized concentration dependence of

this coefficient in a doped semiconductor, respectively; k_i^{HIA} and $k^{HIAC}(\chi)$ are the coefficient of absorption of nonequilibrium hydrogen interstitials, when passivation of impurity atoms occurs in the near intrinsic silicon, and the normalized concentration dependence of this coefficient in a doped semiconductor, respectively.

The empirical parameters β^{HI-} and β^{HI+} describe the relative contribution of negatively and positively charged hydrogen interstitials, respectively, to the total hydrogen diffusion in comparison with the contribution of neutral interstitials. The empirical parameters β^{HIS-} and β^{HIS+} respectively describe the relative absorption of negatively and positively charged hydrogen interstitials due to unsaturated traps in comparison with the absorption of neutral interstitials. At last, the empirical parameter β^{HIA} describes the relative absorption of positively charged hydrogen interstitials during the passivation of electrically active boron atoms in comparison with the absorption of neutral interstitials.

It is important to note that the concentration dependences $d^{HIC}(\chi)$, $k^{HIC}(\chi)$, and $k^{HIAC}(\chi)$ are smooth and monotone functions of χ [8]. In addition, these functions have the form traditionally used for the presentation of effective diffusivity of substitutionally dissolved dopant atoms in processing simulation codes (see, for example, [9]). Due to these features, the system of equations (3), (4), (5), and (6) is very convenient for numerical solution. It is also worth noting that the concentration of charge carriers χ can be calculated either from the assumption of local charge neutrality (10) or, more exactly, from the Poisson equation for electrostatic potential φ.

3 Simulation of hydrogen diffusion and boron passivation

To illustrate the efficiency of the model developed in [3, 4] for describing the hydrogen diffusion and passivation of boron atoms, the simulation results for experimental data of Tong et al. [10] are shown in Figs. 1, 2, 3, 4, and 5. In [10], deuteration was carried out in a theta-pinch plasma or a neutral atom gun. Deuterium profiling was carried out using SIMS with a cesium-ion source. The lower limit of the measurable concentration of deuterium was 10^4 μm^{-3}. The deuteration temperature was chosen to be 200 °C and the surface treatment durations were 5, 10, and 15 minutes.

To obtain the calculated deuteration concentration presented in Figs. 1, 2, 3, 4, and 5, we used an analytical solution of Eq. (6) for the case of the source provides permanent time-independent generation of a slow diffusing hydrogen species in the thin surface layer of silicon substrate. Thus, the flux of the slow component is approximated analytically. The reflecting boundary condition on the semiconductor surface is imposed on the low diffusing species with concentration C^{HD}. It can be seen from the experimental profiles that this type of a boundary condition is in agreement with the shape of hydrogen distribution in the near surface region. On the other hand, the finite-difference method [11] is applied to find a numerical solution for the system of Eqs. (3), (4), and (5). It is supposed that generation of nonequilibrium interstitials occurs due to the plasma immersion ion implantation of hydrogen in the thin surface layer. In addition, the hydrogen interstitials can be generated due to the rearrangement or dissolution of platelets which incorporate hydrogen atoms. Unfortunately, the energy of hydrogen ions was not mentioned in [10]. However, the thickness of the layer where generation occurs is negligible in comparison

with the average migration length of hydrogen interstitials and character dimensions of the passivation region. Therefore, to obtain a numerical solution, the Dirichlet boundary conditions on the surface and in the bulk of the semiconductor are imposed on the rapidly diffusing neutral nonequilibrium deuterium interstitials with concentration $C^{HI\times}$. Numerical computations were carried out on a 1D simulation domain $[0, x_B]$, where x_B and mesh point number were equal to 1.4 μm and 7001, respectively. Also, the time grid with 5000 equal steps was used to obtain a numerical solution.

As can be seen from Fig. 1, the calculated deuterium concentration profile is in good agreement with the experimental data of [10]. The following values of simulation parameters were used to fit the calculated curve to the experimental deuterium concentration profile: $Q_i^{HD} = 1.2\times10^{15}$ cm^{-2}; $D_i^{HD} = 2.0\times10^{-6}$ μm^2/s; $d_i^{HI} = 7.251$ μm^2/s; $l_i^{HI} = 4.2$ μm; $C_S^{HD\times} = 1.02\times10^2$ μm^{-3}; $\beta^{HI-} = 0$; $\beta^{HI+} = 1.0\times10^{-6}$; $\beta^{HIS-} = 0$; $\beta^{HIS+}= 0$; $k_i^{HIA} = 0.21\times10^{-3}$ μm^3/s; $\beta_i^{HIA} = 0.4$; $C_u= 1.3\times10^6$ μm^{-3}. Here Q_i^{HD} is the dose of hydrogen atoms which are responsible for slow diffusing species; $C_S^{HD\times}$ is the concentration of deuterium interstitials in the neutral charge state at the surface; $l_i^{HI} = \sqrt{d_i^{HI}\tau_i^{HI}}$ is the average migration length of hydrogen interstitials in an intrinsic silicon; C_u is the concentration of uniformly distributed boron atoms in a substitutional position before hydrogenation.

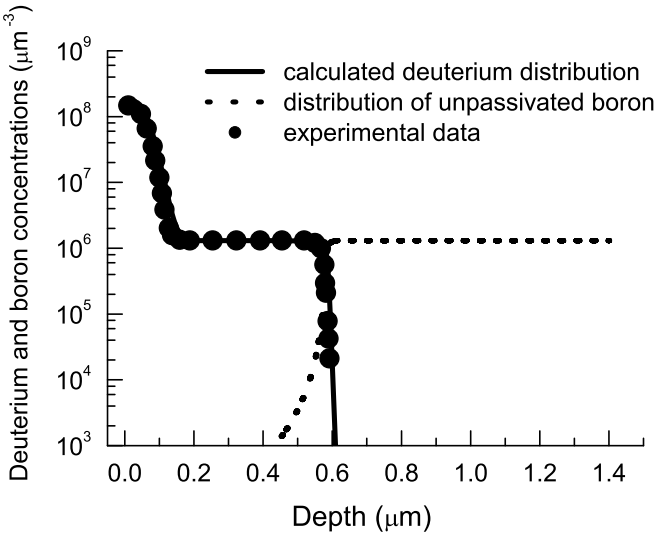

Figure 1: Calculated profiles of the total deuterium concentration (solid line) and unpassivated boron concentration (dotted line) for hydrogenation in the gas discharge plasma at a temperature of 200 °C for 5 min. The experimental data (black circles) are taken from Tong et al. [10].

It follows from the fitting procedure that the increase of k_i^{HIA} or β^{HIA} results in a more abrupt deuterium profile between the passivated and unpassivated regions. The value of hydrogen diffusivity in intrinsic silicon $d_i^{HI} = 7.251$ μm^2/s for a temperature of 200 °C was taken from [7]. Because the average migration length of deuterium interstitials in an intrinsic silicon l_i^{HI} is greater than 1 μm (it can be seen from Fig. 1 that the thickness of intrinsic silicon to the end of the passivation process is greater than 0.4

μm, and the thickness of hydrogenated layer is approximately equal to 0.6 μm), we use in the simulation procedure the value $l_i^{HI} = 4.2$ μm. Then, the average lifetime of the nonequilibrium hydrogen interstitials in an intrinsic silicon τ_i^{HI} is equal to 2.43 s, i.e., τ_i^{HI} is significantly smaller than the duration of hydrogenation (5 min). This value of τ_i^{HI} confirms the correctness of the assumption about the quasistationary distribution of hydrogen interstitials due to their high mobility.

In Fig. 2, the calculated deuterium concentration profile after thermal treatment for 15 minutes is presented. The same values for diffusion of hydrogen interstitials and the same passivation parameters were used in these calculations. As can be seen from Fig. 2, the calculated deuterium concentration profile is in good agreement with the experimental data of [10], as concerns the length of the passivated region. On the other hand, the abruptness of the calculated profile at the boundary between the passivated and unpassivated regions is very high and disagrees with the experimental data. Similar calculations of the deuteration distribution for 10 minutes show that in this case the profile abruptness is also greater in comparison with the experimental one.

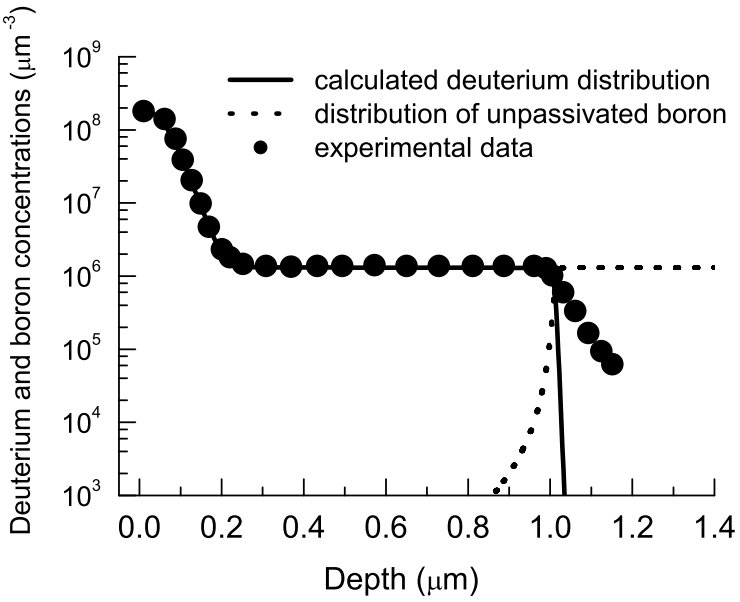

Figure 2: Calculated profiles of the total deuterium concentration (solid line) and unpassivated boron concentration (dotted line) for hydrogenation in the gas discharge plasma at a temperature of 200 °C for 15 min. The experimental data (black circles) are taken from Tong et al. [10].

It is rather difficult to explain the obtained disagreement at the boundary between the passivated and unpassivated regions after plasma treatment for 10 and 15 minutes. Indeed, to reduce the abruptness of the calculated deuterium profile, one can decrease the value of k_i^{HIA} and/or β^{HIA}. In Figs. 2, 4, and 5, the calculated deuterium concentration profiles with $k_i^{HIA} = 0.2{\times}10^{-4}$ μm^3/s and $\beta^{HIA} = 0.12$ a. u. after thermal treatment for 5, 10, and 15 minutes are presented.

It can be seen from Figs. 3, 4, and 5 that the deuterium concentration profile

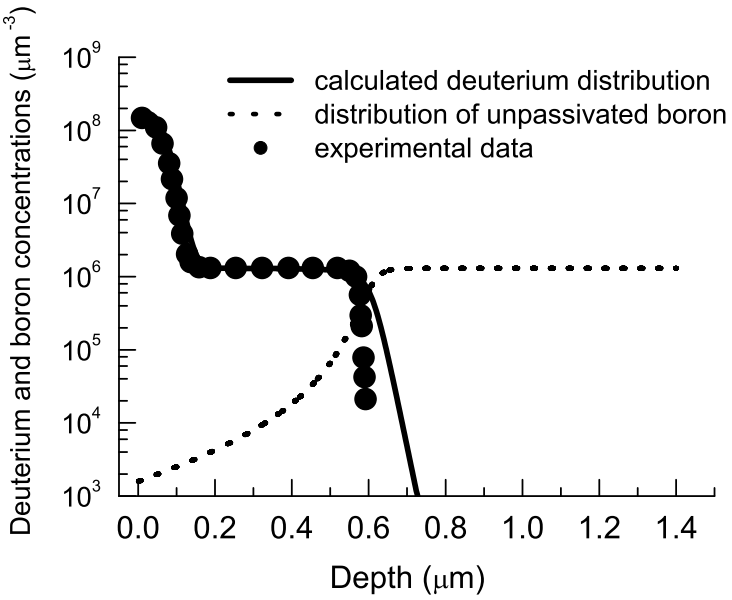

Figure 3: Calculated profiles of the total deuterium concentration (solid line) and unpassivated boron concentration (dotted line) for hydrogenation in the gas discharge plasma at a temperature of 200 °C for 5 min. The decreased values of $k_i^{HIA} = 0.2{\times}10^{-4}$ μm^3/s and $\beta^{HIA} = 0.12$ a. u. are used in simulation of hydrogen diffusion. The experimental data (black circles) are taken from Tong et al. [10].

calculated for the decreased values of k_i^{HIA} and β^{HIA} agree well with the experimental data if plasma treatment lasts for 10 and 15 minutes whereas for the 5-minutes duration the slope of the experimental profile is steeper. At present, we do not know the physical reasons for the decrease in k_i^{HIA} and β^{HIA} with increase in the duration of deuteration and respectively in the depth of the passivated region. Indeed, the reactions between the hydrogen and boron atoms are independent of the distance from the surface. Perhaps, there is an error in the measurements of the deuterium concentration profile, or the nonequilibrium point defects generated in the near surface region due to plasma treatment change the conditions for passivation. For example, generated silicon self-interstitials can kick-out boron atoms from their substitutional position (Watkins effect). This problem requires a further investigation.

It is worth noting that simulation of the experimental data of Tong et al. [10] was also carried out in [6]. The model of hydrogen diffusion proposed in [6] also takes into account two different fluxes of hydrogen species. It is supposed that "fast" diffusion occurs due to the migration of atomic hydrogen in different charge states H^-, $H^\times$, and H^+. To describe "slow" diffusion in the high concentration region, the mechanism of formation and migration of hydrogen complexes with mobile traps generated during plasma treatment is used. It is supposed in [6] that silicon vacancies trap hydrogen atoms and form mobile complexes V-H, which are responsible for the "slow" diffusion. In contrast to the present paper, only one quasichemical reaction, i.e.,

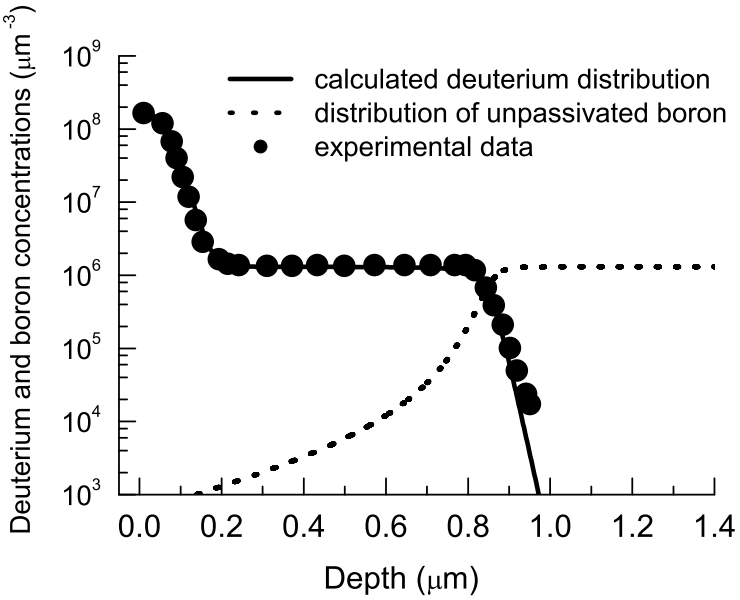

Figure 4: Calculated profiles of the total deuterium concentration (solid line) and unpassivated boron concentration (dotted line) for hydrogenation in the gas discharge plasma at a temperature of 200 °C for 10 min. The decreased values of $k_i^{HIA} = 0.2{\times}10^{-4}$ μm^3/s and $\beta^{HIA} = 0.12$ a. u. are used in simulation of hydrogen diffusion. The experimental data (black circles) are taken from Tong et al. [10].

$$\mathrm{A}^- + \mathrm{H}^+ \leftrightarrows (\mathrm{AH})^\times \,, \tag{12}$$

is used to describe passivation of boron atoms. It is also supposed in [6] that reaction (12) as distinct from reaction (1) is reversible, i. e., the detrapping of hydrogen atoms can occur. On the other hand, it was found in [12] that the dissociation energy of the (BH) complex is equal to 1.28 ±0.03 eV, i.e., it is high enough in comparison with the value of $k_BT = 0.04077$ eV for a temperature of 200 °C. Here k_B is the Boltzmann constant. Therefore, in reactions (1) and (2) the process of detrapping is omitted. As can be seen from the paper of Zhang [6], a full fitting of calculated deuterium concentration profiles to the experimental ones is not achieved, because the abruptness of the calculated deuterium distributions at the boundary between the passivated and unpassivated regions also disagrees with the experimental data. We hope that new, more precise measurements of deuterium distributions in silicon substrates doped with boron can solve this problem.

4 Conclusions

The model of hydrogen migration and reactions of hydrogen atoms with electrically active impurity which had been developed in [3, 4] was applied for simulating the hydrogen diffusion and passivation process during plasma deuteration of silicon substrates uniformly doped with boron. For comparison, the experimental data of Tong et al. [10] for plasma

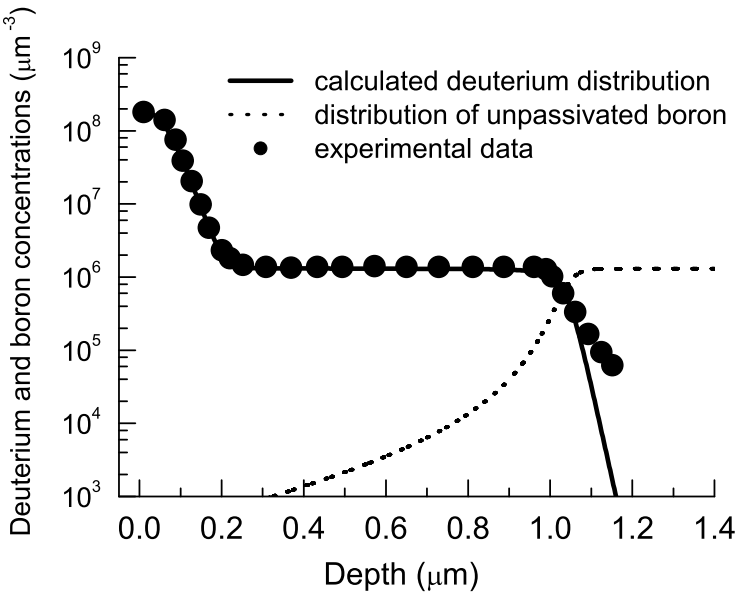

Figure 5: Calculated profiles of the total deuterium concentration (solid line) and unpassivated boron concentration (dotted line) for hydrogenation in the gas discharge plasma at a temperature of 200 °C for 15 min. The decreased values of $k_i^{HIA} = 0.2{\times}10^{-4}$ μm^3/s and $\beta^{HIA} = 0.12$ a. u. are used in simulation of hydrogen diffusion. The experimental data (black circles) are taken from Tong et al. [10].

treatment at a temperature of 200 °C for 5, 10, and 15 minutes was used. The calculated deuterium concentration profiles agree well with the experimental data for the entire time of plasma treatment if we suppose that the coefficient of absorption of hydrogen interstitials in the near intrinsic semiconductor k_i^{HIA} as well the empirical parameter β^{HIA}, which describes the relative absorption of positively charged hydrogen interstitials in comparison with the absorption of neutral interstitials during the passivation of electrically active dopant atoms, are decreased with increase in the duration of deuteration and accordingly in the depth of the passivated region. It is possible that this decreasing occurs due to the nonuniform spatial distribution of nonequilibrium point defects, which are generated during plasma treatment and can influence the passivation process. If the invariable values of the simulation parameters are used for different durations of plasma treatment, the calculated deuterium concentration profile is in good agreement with the experimental data of [10], as concerns the length of the passivated region. However, the abruptness of the deuterium concentration profiles at the boundary between the passivated and unpassivated regions disagrees with the experimental data either with treatment for 5 minutes or 10 and 15 minutes.

References

[1] T. Saga, Advances in crystalline silicon solar cell technology for industrial mass production, NPG Asia Mater. Vol.2, No.3. pp. 96-102 (2010).

[2] M.A. Green, K. Emery, Y. Hishikawa, W. Warta, E.D. Dunlop, Solar cell efficiency tables (version 39), Progress in Photovoltaics: Research and Applications. Vol.20, No.1. pp.12-20 (2012).

[3] O.I. Velichko, Modeling of passivation of electrically active impurities by hydrogen atoms, In: Proc. of the 8-th Int. Conf. "Interaction of Radiation with Solids", September 23-25, 2009, Minsk, Belarus. pp.154-156 (2009).

[4] O.I. Velichko, Yu.P. Shaman, Interstitial diffusion under conditions of trapping of interstitial impurity atoms, Mater. Sci. Semicond. Process. No.13. pp.13-20 (2010).

[5] R Rizk, P. de Mierry, D. Ballutaud, M. Aucouturier, D. Mathiot, Hydrogen diffusion and passivation processes in p- and n-type crystalline silicon. Phys. Rev. B. Vol.44. pp.6141-6151 (1991).

[6] Yi. Zhang, Modeling hydrogen diffusion for solar cell passivation and process optimization. PhD dissertation. New Jersey Institute of Technology and Rutgers, the State University of New Jersey-Newark (2002).

[7] A. Van Wieringen, N. Warmoltz, On the permeation of hydrogen and helium in single crystal silicon and germanium at elevated temperatures, Physica. Vol.22. pp.849-865 (1956).

[8] O.I. Velichko, Atomic diffusion processes under nonequilibrium state of the components in a defect-impurity system of silicon crystals. Ph.D. theses, Institute of Electronics of the National Academy of Sciences of Belarus, Minsk (1988) (in Russian).

[9] *ATHENA User's Manual*. (SILVACO, Inc. Santa Clara, CA, 2012) 432 p. www.silvaco.com

[10] B.Y. Tong, X.W. Wu, G.R. Yang, S.K. Wong, A study of hydrogen diffusion in crystalline silicon by secondary-ion mass spectrometry, Can. J. Phys. Vol.67. pp.379-383 (1989).

[11] A.A. Samarskii, *The theory of difference schemes* (Marcel Dekker Incorporated, 2001).

[12] T. Zundel, J. Weber, Dissociation energies of shallow-acceptor-hydrogen pairs in silicon, Phys. Rev. B. Vol.39, No.18. pp.13549-13552 (1989).